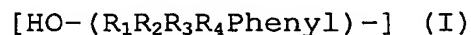


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ART 34 AMDTClaims

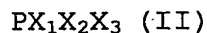
1. A stabilized polymer composition comprising a polymer  
and an antioxidant composition for improving the long term  
5 heat stability of polymers, in particular polyolefins, said  
antioxidant composition comprising:

(a) 0,01% - 0,5% by weight of at least one sterically  
hindered phenolic compound, wherein said phenolic compound  
contains at least one phenolic moiety of general formula (I):



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> may be the same or different and at  
least one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> is selected from the group  
15 consisting of branched alkyl having 1 to 12 carbon atoms,  
preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl  
and adamantyl, the others of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> being H or lower  
alkyl having 1 to 6 carbon atoms;

20 (b) 0,01% - 0,5% by weight of at least one phosphorous  
compound, wherein said phosphorous compound contains at least  
one phosphorous compound moiety of general formula (II):



wherein X<sub>1</sub> may be R<sub>5</sub> or OR<sub>5</sub>, X<sub>2</sub> may be R<sub>6</sub> or OR<sub>6</sub>, X<sub>3</sub> may be R<sub>7</sub>  
or OR<sub>7</sub> and R<sub>5</sub>, R<sub>6</sub> or R<sub>7</sub> may be the same or different and at  
least one of R<sub>5</sub>, R<sub>6</sub> or R<sub>7</sub> is selected from the group  
consisting of C<sub>1</sub>-C<sub>25</sub> alkyl group, aryl group or aralkyl group  
30 which may be substituted by lower alkyl having 1 to 6 carbon  
atoms, or two or any of R<sub>5</sub>, R<sub>6</sub> or R<sub>7</sub> may form a ring structure  
having 4 to 12 carbon atoms,

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



5

wherein  $x = 1$  or  $2$ , and wherein  $R_8$  and  $R_9$  may be the same or different and are selected from the group consisting of  $C_{10}$ - $C_{25}$  alkyl groups optionally being substituted with  $C_1$ - $C_{12}$  alkyl ester carboxylates,

10 wherein said % by weight values are referred to the polymer composition.

2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, 15 wherein said antioxidant composition comprises:

(a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

(b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

20 (c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer composition.

25 3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

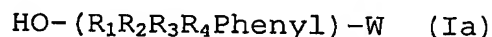
(a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

30 (b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),

wherein said % by weight values are referred to the polymer composition.

4. The stabilized polymer composition of any of claims 1 to 3, wherein the phenolic compound contains at least one phenolic moiety of general formula (Ia):



10 wherein  $\text{R}_1$  and  $\text{R}_4$  being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched  $\text{C}_1$  to  $\text{C}_{12}$  alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues,  $\text{R}_2$  and  $\text{R}_3$  having the meaning as given  
15 before, and  $\text{W}$  is selected from  $\text{C}_1$  to  $\text{C}_{12}$  alkyl,  $\text{C}_1$  to  $\text{C}_{12}$  alkoxy,  $\text{C}_1$  to  $\text{C}_{12}$  alkyl carboxylate or  $\text{C}_1$  to  $\text{C}_{12}$  alkyl substituted by another group of the formula  $\text{HO}-(\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{Phenyl})-$ , wherein  $\text{R}_1$  to  $\text{R}_4$  have the meaning as indicated before.

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5. The stabilized polymer composition of any of claims 1 to 4, wherein the phosphorous compound comprises a phosphite moiety of the formula  $\text{Bis}(\text{R}_{10})$ -pentaerythrityldiphosphite, wherein  $\text{R}_{10}$  is selected from  $\text{C}_1$ - $\text{C}_{25}$  alkyl group or aryl group  
25 which may be substituted by lower alkyl having 1 to 6 carbon atoms.

6. The stabilized polymer composition of any of claims 1 to 5, wherein the sulphur-containing compound of general  
30 formula (III):



is selected from  $\text{Di}(\text{C}_1\text{-C}_{20})\text{alkyl-(S)}_x\text{-di-carboxylate}$  wherein the carboxylic acid is selected from  $\text{C}_1$  to  $\text{C}_{12}$  alkyl carboxylic acids.

- 5           7. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:
- 2,6-Di-tert.-butyl-4-methyl phenol;
  - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-
  - 10 hydroxyphenyl)-propionate;
  - Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
  - 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
  - 15 - 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;
  - Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethylphosphonate);
  - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
  - 20 isocyanurate;
  - Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic acid)-glycolester;
  - 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
  - 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);
  - 25 - N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-hydrocinnamamide;
  - 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl) chroman-6-ol;
  - 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);
  - 30 - 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl)butane;
  - 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;

- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis(4-methyl-6-tert.-butylphenol);
- 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl))propane;
- Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C<sub>13</sub>-C<sub>15</sub>-branched and linear alkyl esters;
- 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)4-hydroxy-, C<sub>7</sub>-C<sub>9</sub>-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
- Butylated reaction product of p-cresol and dicyclopentadiene.

8. The stabilized polymer composition of any of the precedent claims, wherein the phosphorous compound is selected from the group consisting of:

- Tris(2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-*t*-butylphenyl)-4,4'-biphenylen-di-phosphonite
  - Bis (2,4-di-*t*-butylphenyl)-pentaerythrityl-di-phosphite;
- 5     - Di-stearyl-pentaerythrityl-di-phosphite;
- Tris-nonylphenyl phosphite;
- Bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 10    - 2,2'-Methylenebis (4,6-di-*t*-butylphenyl) octyl-phosphite;
- 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-*t*-butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-*t*-butylphenyl-di-tridecyl) phosphite;
- 15    - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-*t*-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- 20    - - Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-*t*-butylphenyl ester; Bis (2,4,6-tri-*t*-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-*t*-butylphenyl) fluorophosphonite
- 25    - 6- (3-*tert*-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-*tert.* butyldibenz (d,t) (1.3.2) dioxaphosphopin; and
- Tetrakis-(2,4-di-*t*-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite.

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9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- 5 - Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- 10 - Pentaerythritol-tetrakis-(3-laurylthiopropionate)

10. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 15 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 20 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 25 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane.

30 11. The stabilized polymer composition of any of the preceding claims, wherein the phosphite compound is selected from the group consisting of:

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;

- Bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- Di-stearyl-pentaerythrityl-di-phosphite; and
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

5

12. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is Di-stearyl-thio-di-propionate or Di-tert-dodecyl-disulphide.

10

13. The stabilized polymer composition of any of any of the preceding claims, wherein

(a) the sterically hindered phenolic compound is 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;

15

(b) the phosphite compound is bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and

(c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

20

14. The stabilized polymer composition of any of claims 1-13, wherein said composition further comprises metal deactivators and/or UV-stabilisers.

25

15. The stabilized polymer composition of claim 14, wherein said UV-stabilizers are sterically hindered amines.

16. The stabilized polymer composition of any of claims 1-16 wherein said polymer is selected from the group consisting of polyolefins, polyethers, polyimides, polyamides and polyesters or mixtures thereof.

30



17. The stabilized polymer composition of claim 16, wherein said at least one polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 18. Use of the antioxidant composition as defined in any of claims 1-14 for reducing degradation of a polymeric material during processing and end use of said polymeric material.

10 19. The use of claim 18 for increasing long term thermal stability of the polymeric material.

20. Method for producing a polymeric article having an improved long term thermal stability against ageing by  
15 radical degradation processes comprising the steps of:  
    (a) providing an unstabilised base polymer material;  
    (b) adding to said base polymer material the antioxidant composition as defined in any of the preceding claims;  
    (c) converting the composition obtained in step (b) in a  
20 melt-forming process; and  
    (d) confectioning the polymeric material obtained in step (c).

21. The method of claim 19 further comprising adding  
25 other stabilisers and/or modifiers before the converting step c).

22. The method of any of claims 20 or 21, wherein the converting step includes injection moulding, blow moulding,  
30 rotational moulding and extrusion.

23. The method of any of claims 20 to 22, wherein the confectioning step includes cutting, lamination and/or welding.

24. Polymeric article having an increased long term ageing stability obtained by the method of any of claims 20-23.